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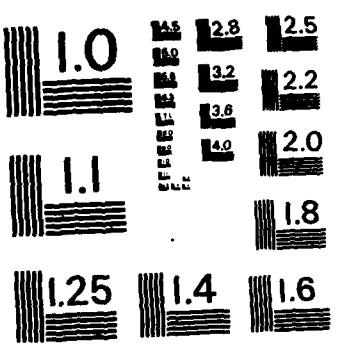

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COMPARISON OF JFTOT AND ABSORBANCE METHODS FOR DETERMINING JET FUEL THERMAL STABILITY

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Canada

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ABSTRACT

The thermal stabilities of five aviation turbine fuels were examined employing the Jet Fuel Thermal Oxidation Tester (JFTOT) and an optical absorbance method based on the Phillips 5 ml bomb test.

No correlation was observed between the ranking of the fuels by the two methods.

RÉSUMÉ

La stabilité thermique de cinq carburéacteurs a été examinée au moyen d'essais d'oxydation thermique de carburéacteurs (EOTCR) et d'une méthode d'absorbance optique basée sur l'essai à la bombe de 5 ml Phillip.

Aucune corrélation entre des carburants de différentes qualités n'a été observée par les deux méthodes.

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1.0 INTRODUCTION

A previous note [1] described attempts to employ the optical absorbance changes that result from heat stressing of a jet fuel as a measure of its thermal stability. The effects of a number of contaminants and commercial fuel additives were studied. A procedure was used to characterize fuel stability in terms of a breakpoint, the characteristic temperature for a given increase in absorbance in a standardized heating experiment; this was suggested by and modelled on the Phillips 5 ml bomb test [2]. A number of perturbing effects were found, ascribable to fuel additives, which suggested that optical methods might be only of restricted use in this role.

The Jet Fuel Thermal Oxidation Tester (JFTOT) is the standard and most widely used method for determining jet fuel stability in practice [3]. As a JFTOT was available it was decided to complete the investigation with a direct comparison of these two methods, using the available jet fuels.

Five fuels were examined, using a breakpoint determination with both methods so as to get a comparative rating of stability in as quantitative terms as possible. A variation was introduced by subjecting all fuels to clay filtering and then re-testing.

Clay filtering, which preferentially absorbs polar molecules, will remove polar nitrogen, oxygen and sulfur compounds, some of them detrimental to thermal stability; and also the fuel additives. The principal additives in use are: antioxidants, a blend of phenylene-diamines and hindered phenols in varying proportions; metal deactivator, whose function is to chelate metallic ions, particularly copper, which can participate in chain oxidative reactions; and anti-corrosion agents containing long chain fatty acid derivatives. All of the above being polar will be taken out in varying degrees by clay filtering. Fuels produced to military specifications will in addition contain fuel system icing inhibitor. The effects of several of these additives on absorbance behaviour of the heated fuel were examined briefly in the previous note.

2.0 EXPERIMENTAL

2.1 Absorbance Changes

The procedure for determining absorbance changes in fuels under heat stress has already been described in detail [1]. In summary, the samples were sealed in glass vials, heated under the chosen conditions in a mechanical convection oven, quenched in cold water, and the absorbance at 340 mμ read against a hexane reference. In the modification of the Phillips 5 ml method, which was also described, a supply of some 15-20 samples of a fuel were sealed in vials. The vials (in duplicate) were placed in the oven preheated to a set temperature, and removed and quenched after exactly 30 minutes, the final temperature attained by the vials being defined as the test temperature. Absorbances were read, and the test repeated at a succession of increasing temperatures. The absorbance of the original fuel was subtracted from each reading. From a plot of absorbance increase (Δ absorbance) against test temperature the breakpoint temperature (to a Δ absorbance of 0.05 or 0.100) was obtained by interpolation.

In the Phillips method on which this was based, the sample, enclosed in a metal bomb, was heated in a furnace for 20 minutes, and transmittance, at one of several wave lengths chosen in the range 340-360 mμ, was determined as a function of furnace temperature. Isooctane was used as reference fluid; setting its transmittance at 100%, the breakpoint was defined as the temperature required to reduce transmittance of the heated fuel by 10%, or 25% from its original value (correponding to an absorbance increase of 0.045 or 0.125, and therefore comparable to the 0.050 or 0.100 used here). If the curve ΔT% - temperature was not linear, or was irregular, curve - fitting and statistical procedures were resorted to.

3.0 JFTOT

An outline of the JFTOT procedure was given in the previous note. The stability of the fuel is assessed from the nature of the deposits formed on a heated polished aluminum tube as the air-saturated fuel is passed over it under specified conditions. ASTM Test Method D 3241 [3] describes in elaborate detail the basic method of conducting a fuel thermal stability test with the instrument. For specification purposes, i.e. pass or fail testing, the experiment is run at 260°C for 2.5 hours, and the heater tube is compared visually with a set of colour standards. As used here in breakpoint determinations, runs of the prescribed length were carried out with the fuel at a series of temperatures. The heater tube from each test was examined over its length in the Alcor Mk 8A TDR* which provides a photometer reading related to the intensity of deposit colour on the tube. Maximum TDR readings were plotted as a function of temperature, and by interpolation the temperature found at which this maximum reached 15 scale divisions. This temperature is then the JFTOT breakpoint, the temperature at which the agreed-on failure level is just reached at the end of a full 2.5 hour test.

Use of the Mk 8A TDR as an alternative to the visual colour standards in specification testing has been proposed, with various readings in the general range 13-19 as a criterion of failure, but this has not yet been accepted as a test procedure. The TDR has been used however in a number of non-routine investigations e.g. [4, 5] with readings in this range as a criterion of failure, in order to provide a more quantitative and objective result.

Several refinements have been introduced into the procedure. Calibration of the Mk 8A TDR implicitly assumes a TDR reading of zero for the fresh aluminum surface. This is generally not the case, and it is necessary to record the TDR for the fresh tube, and determine the difference between initial and final TDR's, that is, a ΔTDR [6]. Initial tube readings are frequently below zero on the instrument meter; then a second volt meter must be inserted in parallel to extend the range and record these negative baseline readings.

For the same fuel these two breakpoint temperatures are of course in no way related. What is of concern is whether the two methods rate the

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*An accessory to the JFTOT, supplied by Alcor Inc., the producers of JFTOT.

fuels in the same order, and whether modification of a fuel (as here by clay filtering) shifts the two breakpoints in the same direction.

3.1 Fuels

The five fuels employed were:

1062 - A commercial Jet A-1.

1091 - A Jet A-1 meeting specification requirements but without additives.

1075 - A commercial Jet B, known to have suffered contamination before receipt, and of marginal thermal stability. Testing at the specification temperature of 260°C resulted in a marginal pass or fail, TDR maxima taken at various times being in the range 5-14, which reflects the inherent variability of the measurement.

1092 - A commercial JP-5.

1005 - A commercial Jet B.

Experiments were conducted with a single homogeneous batch of each fuel, stored in thoroughly cleaned amber glass bottles, to minimize risk of deterioration during the series of tests, which were carried out over a period of a few weeks.

3.2 Clay Filtering

Fuels were percolated through an attapulgus clay* column 4 cm in diameter by 8 cm long, contained between two glass wool plugs. A batch of 4.5 litres required approximately one hour to pass through the column.

This treatment resulted, with all fuels except the additive-free 1091, in a noticeable fall in absorbance at 340 mμ, as shown in Table 1.

TABLE 1 - EFFECT OF CLAY FILTERING ON ABSORBANCE

	ABSORBANCE				
	1062	1091	1075	1092	1005
Initial	.179	.127	.195	.274	.085
Clay filtered	.146	.125	.110	.225	.076

This was not suprising, as, apart from any absorbant impurities that may be removed, the antioxidant is intensely coloured. In separate

*Catalog No. 105-99-5116, a product of Emcee Electronics, Venice, Florida.

experiments it was found that addition of a typical antioxidant, 733 PDA 50*, to fuel 1091 at 25 mg/l, in the range commonly used, raised the absorbance from .127 to .236; hence the observations of Table 1 can be explained as anti-oxidant removal from these fuels.

4.0 RESULTS

4.1 JFTOT

A typical set of TDR curves at several temperatures for 1062, before clay filtering, is depicted in Fig. 1(a), the abscissa being the distance in mm measured along the exposed portion of the heater tube and the ordinate the corresponding ΔTDR response. The maximum ΔTDR reading as a function of temperature is plotted in Fig. 1(b), and from the intercept with the horizontal line representing ΔTDR = 15 the breakpoint is 302°. Breakpoint plots for all 10 fuel variations (5 fuels, filtered and unfiltered) are shown in Figs. 2-4, and the data is collected in Table 2, for comparison with absorbance results.

TABLE 2 - JFTOT BREAKPONTS

	1062	1091	1075	1092	1005
Initial	302	272	261	285	301
Clay filtered	298	291	278	281	305

4.2 Breakpoint by Absorbance

In Figs. 5 to 9 are plotted absorbance changes for each of the five fuels, before and after clay filtering, as a function of temperature. Recourse was had to several types of curve fitting to get the best representation of the data; for all curves the exponential expression $y = ae^{bx}$ was the most satisfactory, as judged by values of the coefficient of determination, a measure of goodness of fit; although in most cases if the curves were simply fitted to the points by eye the difference in the breakpoints obtained did not amount to more than 1°C. In each figure the a and b factors and the breakpoints are recorded, and the latter values are collected in Table 3.

*Provided through the courtesy of Ethyl Canada.

TABLE 3 - BREAKPOINTS BY ABSORBANCE

	1062		1091		1075		1092		1005	
Δ absorbance	0.05	0.100	0.05	0.100	0.05	0.100	0.05	0.100	0.05	0.100
Initial	158	164	144	154	132	146	125	133	132	139
Clay Filtered	162	173	142	151	166	170	122	129	137	146

The comparison of results by the two methods is summarized in Figs. 10(a) and 10(b). In Fig. 10(a) the JFTOT breakpoints for the unfiltered fuels are plotted on the left hand ordinate and are linked by straight lines with the breakpoints by absorbance (Δ absorbance = 0.100) for the same fuels on the right hand ordinate. Figure 10(b) is a corresponding plot for the clay-filtered fuels. It is apparent that in neither figure is there any correlation between JFTOT and absorbance results, the rankings being completely different. Similar results are obtained if the plot is made using the absorbance breakpoint criterion of 0.05.

Figures 11(a) to 11(c) display in similar fashion the effects of clay filtering on breakpoints by the individual methods - JFTOT, and the two Δ(absorbance) criteria. The one point of resemblance is that, by all three methods, clay filtering of the contaminated 1075 led to a remarkable elevation of breakpoint. No other similarity is found, the improvement in JFTOT breakpoint on clay filtering of 1091 not being observed in Figs. 11(b) or 11(c). JFTOT results with the remaining three specification fuels, (1092, 1062, 1005) with improvement or deterioration of, as it happens, 4°C in each case, are really within the limit of resolution of the method, and show that a specification fuel with breakpoint well above 260°C is not affected significantly by this treatment. For such fuels, probably, the metal deactivator and antioxidant introduced by the additive treatment sequester or prevent formation of deleterious species; and the reason for the improvement effected in 1091 by clay filtering is precisely that, lacking this protection, such products have had an opportunity to form, so that on longer storage progressive deterioration might be expected. The breakpoint of 1091 before clay filtering is significantly lower than those of 1092, 1005 or 1062.

5.0 SUMMARY

Examination of these results lends added support to the earlier conclusion that optical absorbance is not a useful method for estimating resistance of a jet fuel to thermal stress. This is shown particularly by the failure to find any correlation with results by the JFTOT, which measured degradation by the actually harmful consequence, the formation of solid deposit.

6.0 REFERENCES

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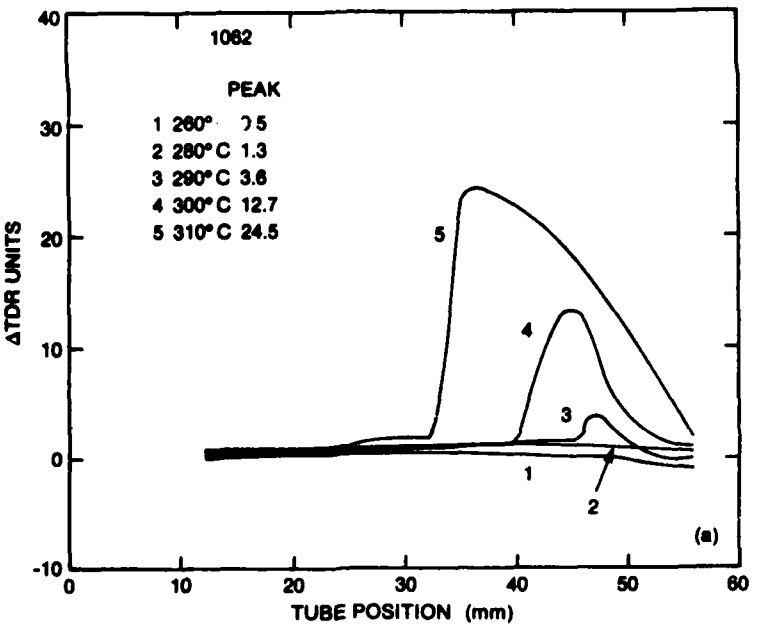
[3] American Society for Testing and Materials. Annual Book of ATSM Standards, Part 25, D3241, "Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)".

[4] Reynolds, T.W., "Thermal Stability of Some Aircraft Turbine Fuels Derived from Oil Shale and Coal", NASA TM X 3551, June 1977.

[5] Martel, C.R., Bradley, R.P., McCoy, J.R. and Petrarca, J. "Aircraft Turbine Engine Fuel Corrosion Inhibitors and Their Effects on Fuel Properties", AFAPL-TR-74-20, July 1974.

[6] Tackett, L., and Bradley, R.P., "Determination of the Effect of Pretest Ratings of Jet Fuel Thermal Oxidation Tester Tubes on Post-Test Ratings using the Tubing Deposit Rater", AFAPL-TR-77-53, June 1977.



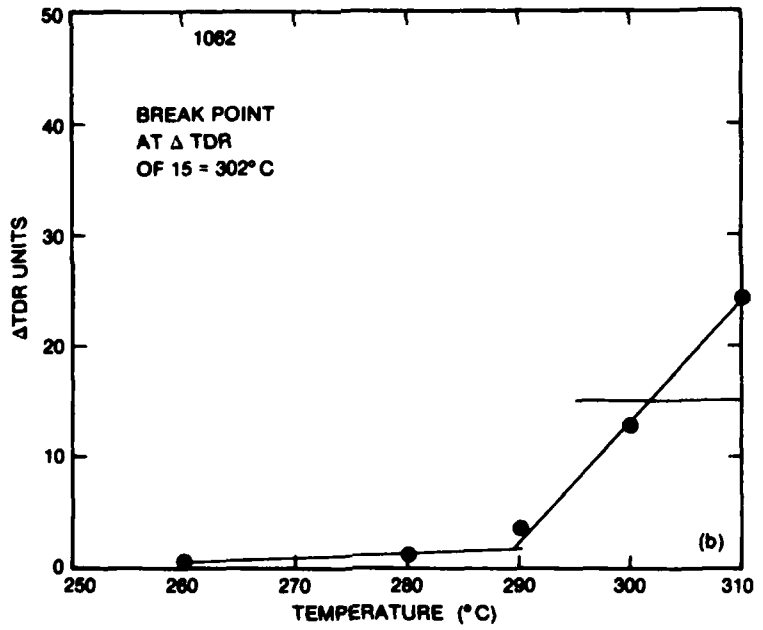


FIGURE 1 - (a) ΔTDR Reading as a Function of Position on Heater Tube, Fuel 1062 as Received (b) Plot of ΔTDR Maxima from 1(a) as a Function of Temperature, JFTOT Breakpoint at 302°C

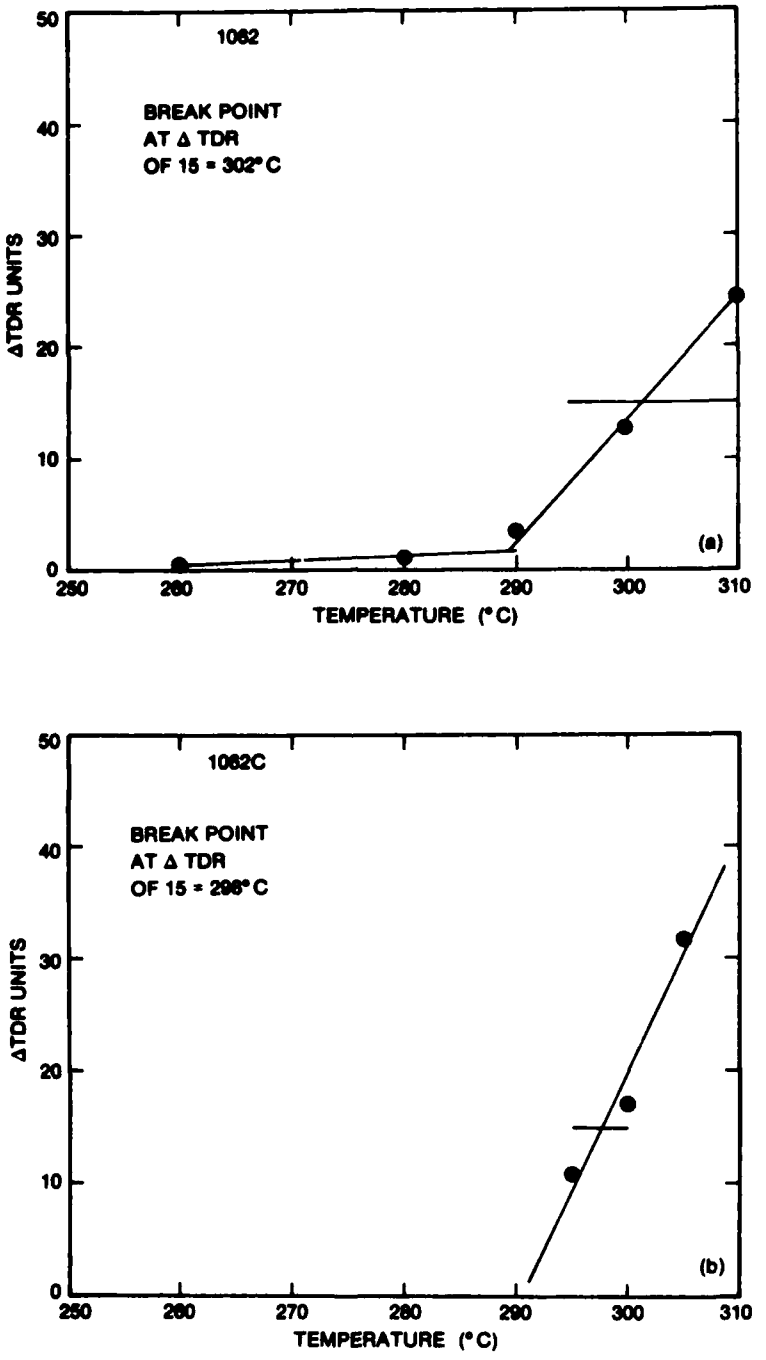
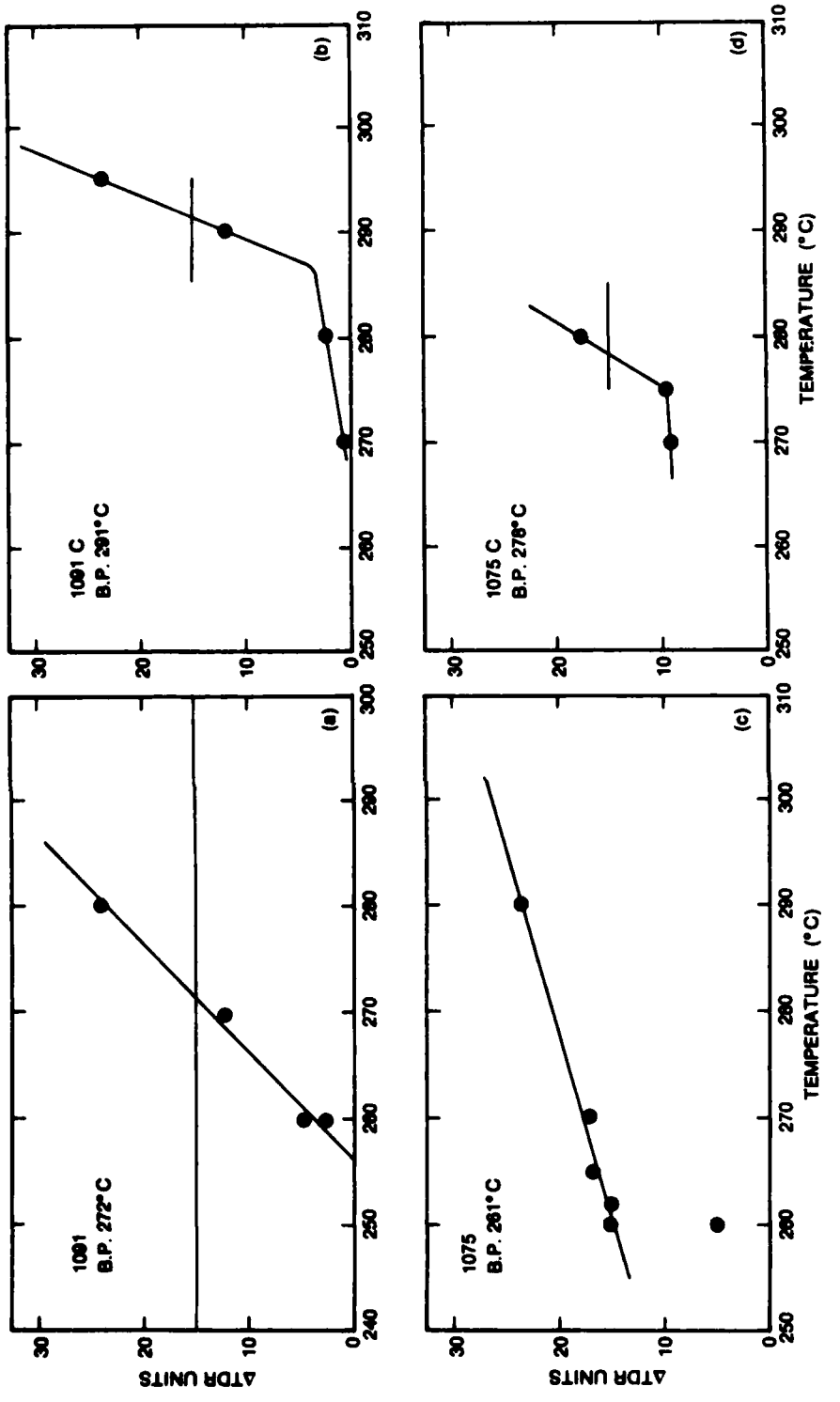


FIGURE 2 - (a) Repetition of Fig. 1(b) JFTOT Breakpoint Plot of Fuel 1062 as Received (b) JFTOT Breakpoint Plot of Fuel 1062 After Clay Filtering



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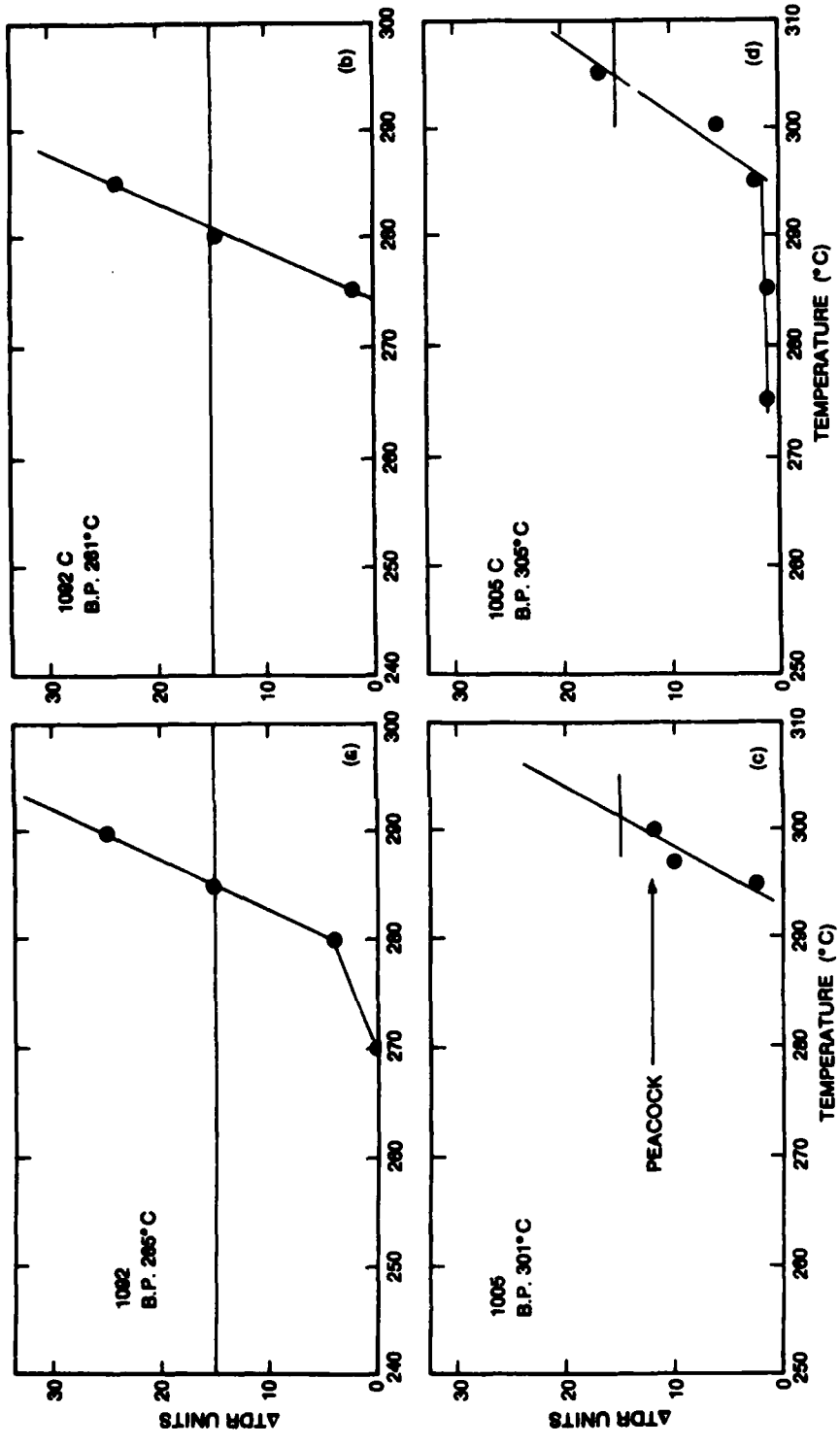


FIGURE 4 - (a) JFTOT Breakpoint Plot of Fuel 1092 as Received (b) JFTOT Breakpoint Plot of Fuel 1092 After Clay Filtering (c) JFTOT Breakpoint of Fuel 1005 as Received (d) JFTOT Breakpoint Plot of Fuel 1005 After Clay Filtering

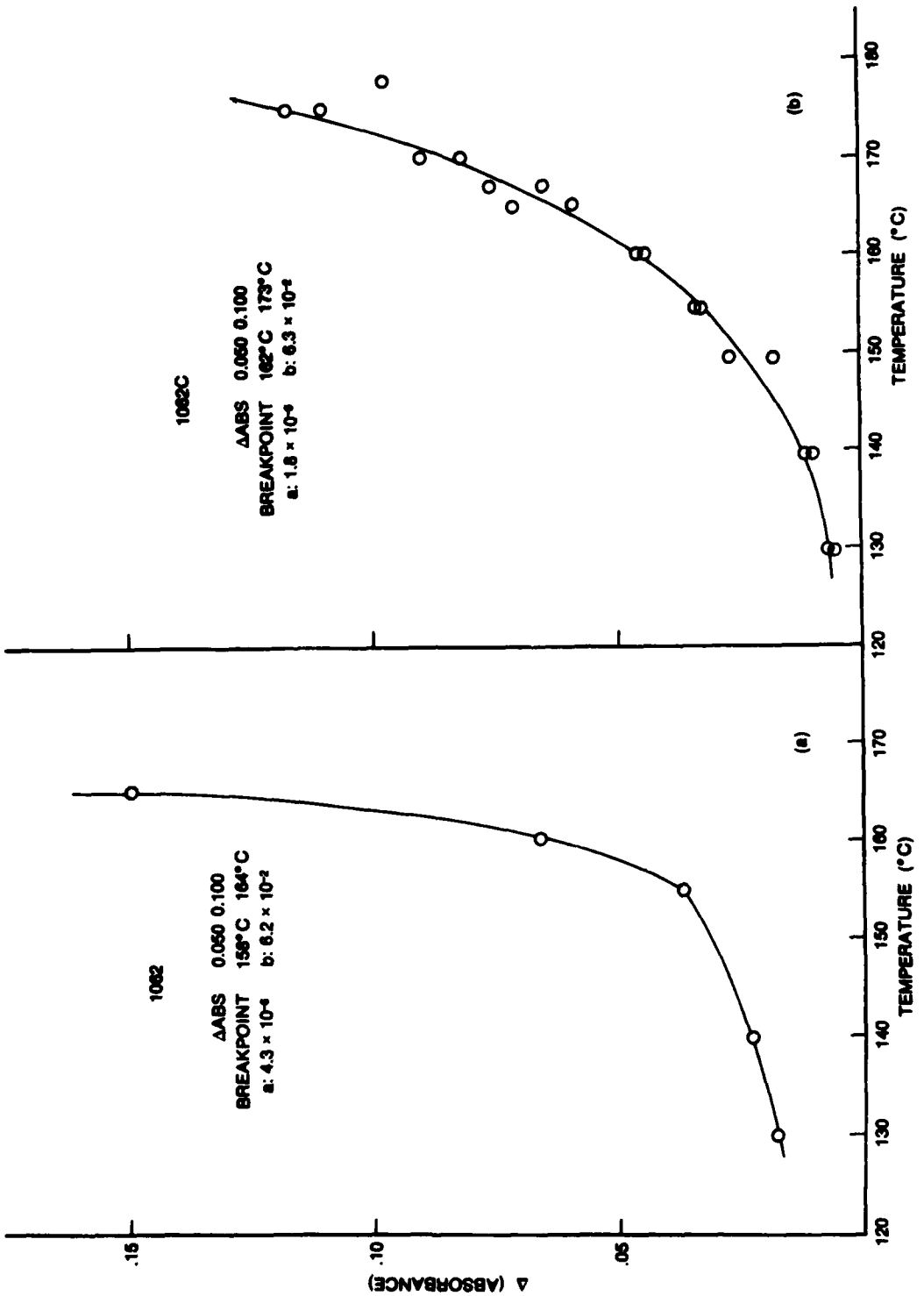


FIGURE 5 - (a) Plot of Absorbance Increase for Fuel 1062 as Received, as Function of Temperature. Line Derived from Plot $y = ae^{bx}$ where y = Δ(absorbance), x = temperature °C. Values for a and b, and Temperatures for Δ(absorbance) = 0.050 and 0.100 are shown in Figure (b) As Fig. 5(a) for 1062 After Clay Filtering

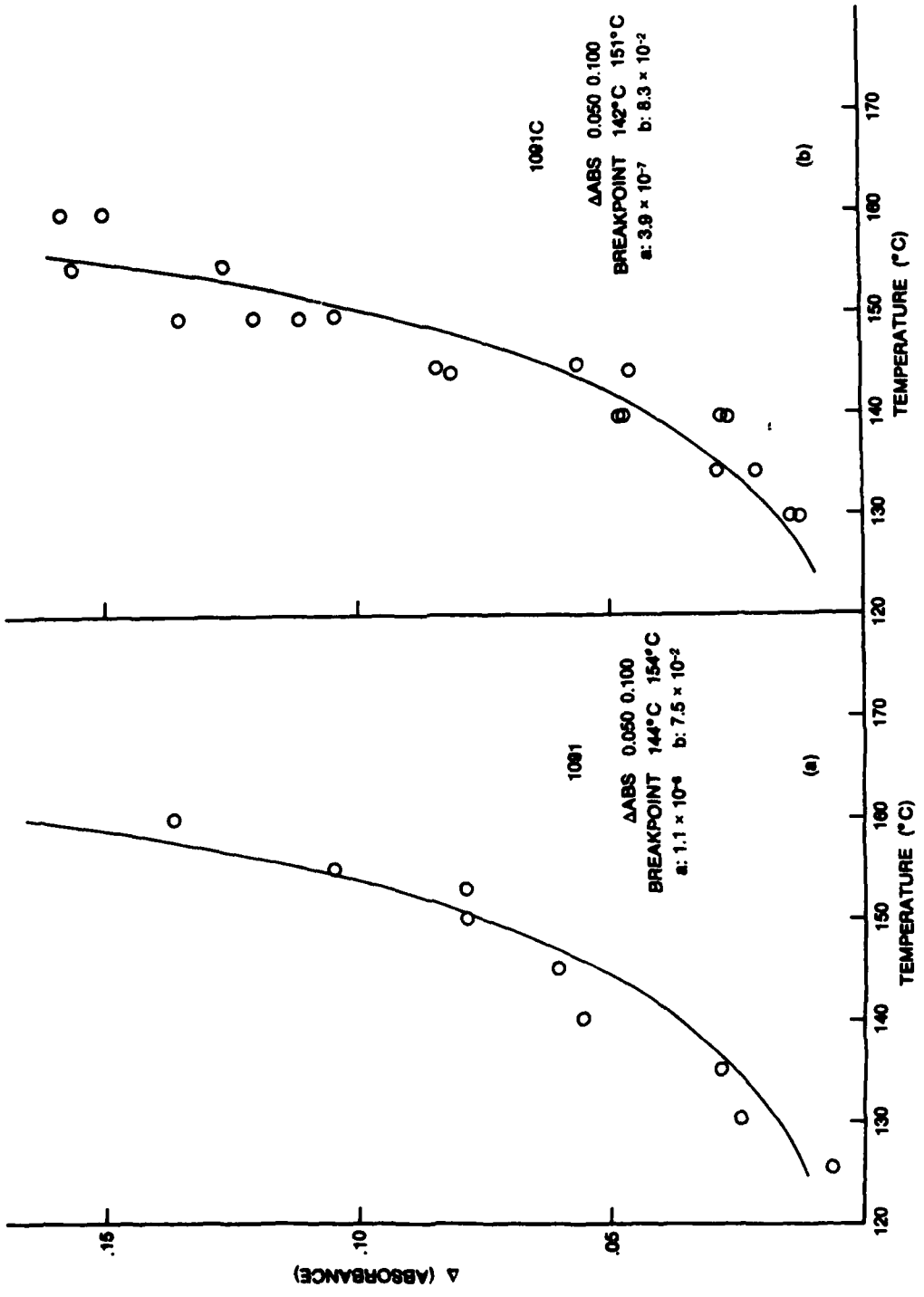


FIGURE 6 - (a) As Fig. 5(a) for 1091 as Received (b) As Fig. 5(a) for 1091 After Clay Filtering

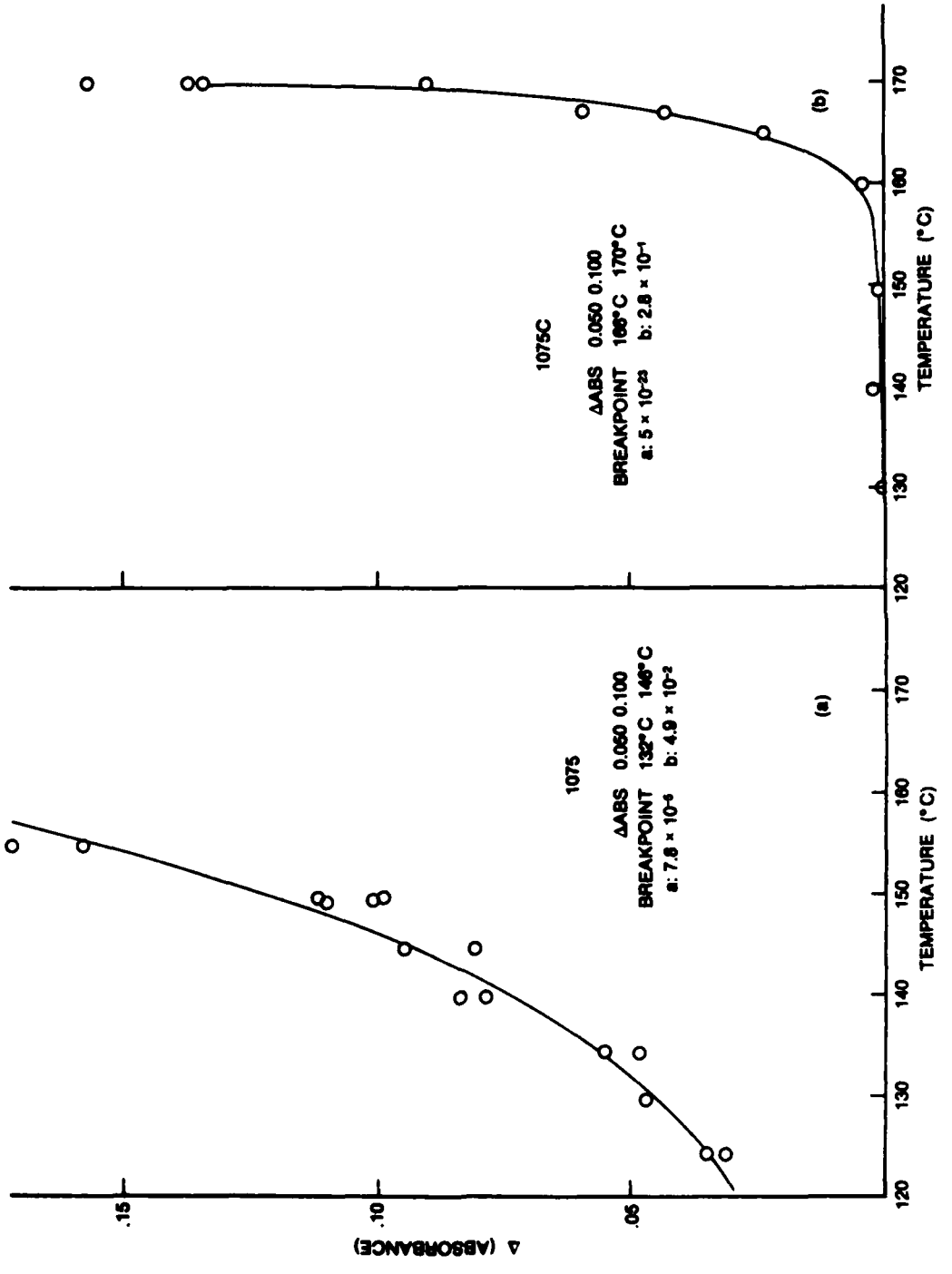


FIGURE 7 - (a) As Fig. 5(a) for 1075 as Received (b) As Fig. 5(a) for 1075 After Clay Filtering

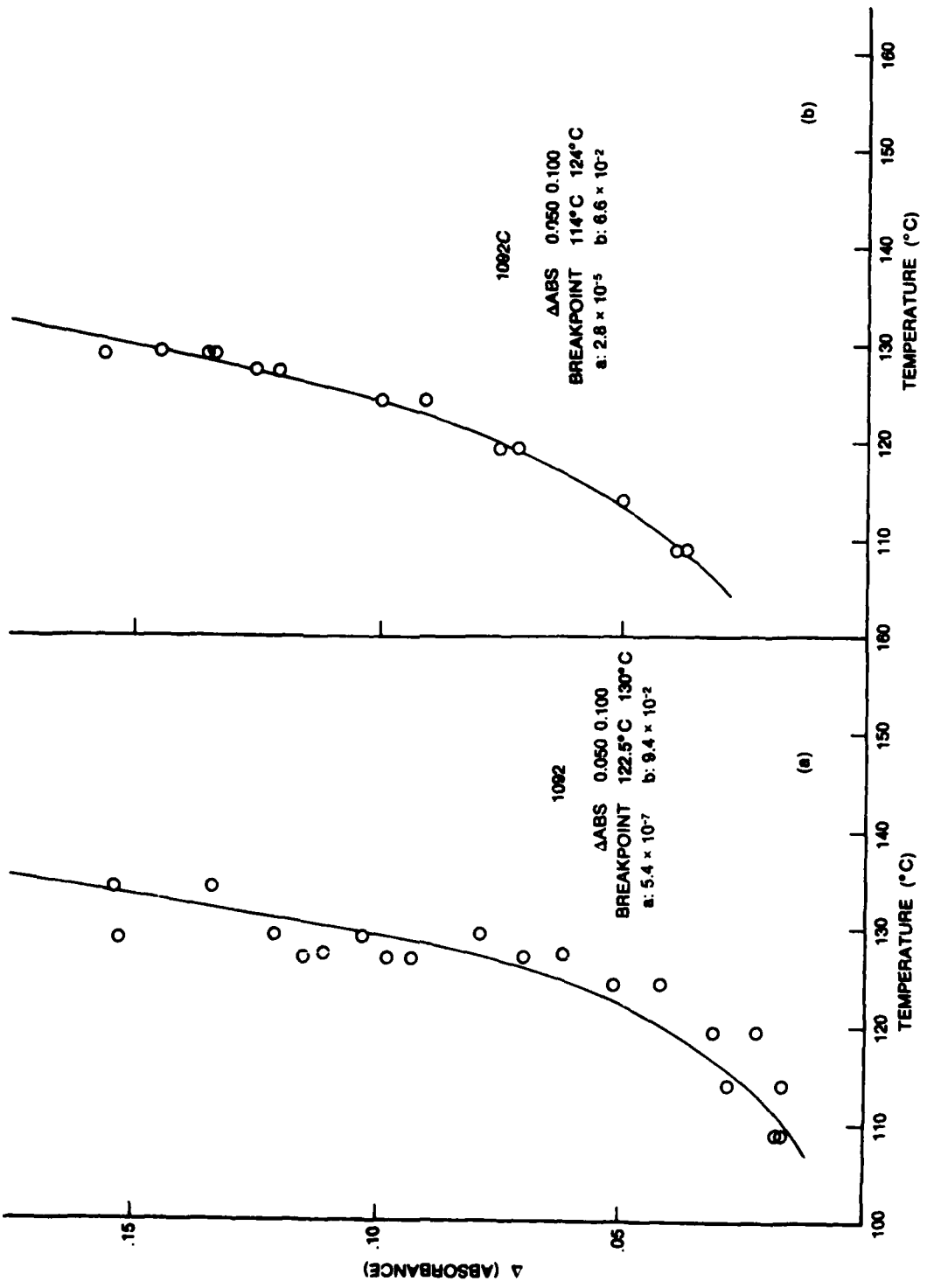


FIGURE 8 - (a) As Fig. 5(a) for 1092 as Received (b) As Fig. 5(a) for 1092 After Clay Filtering

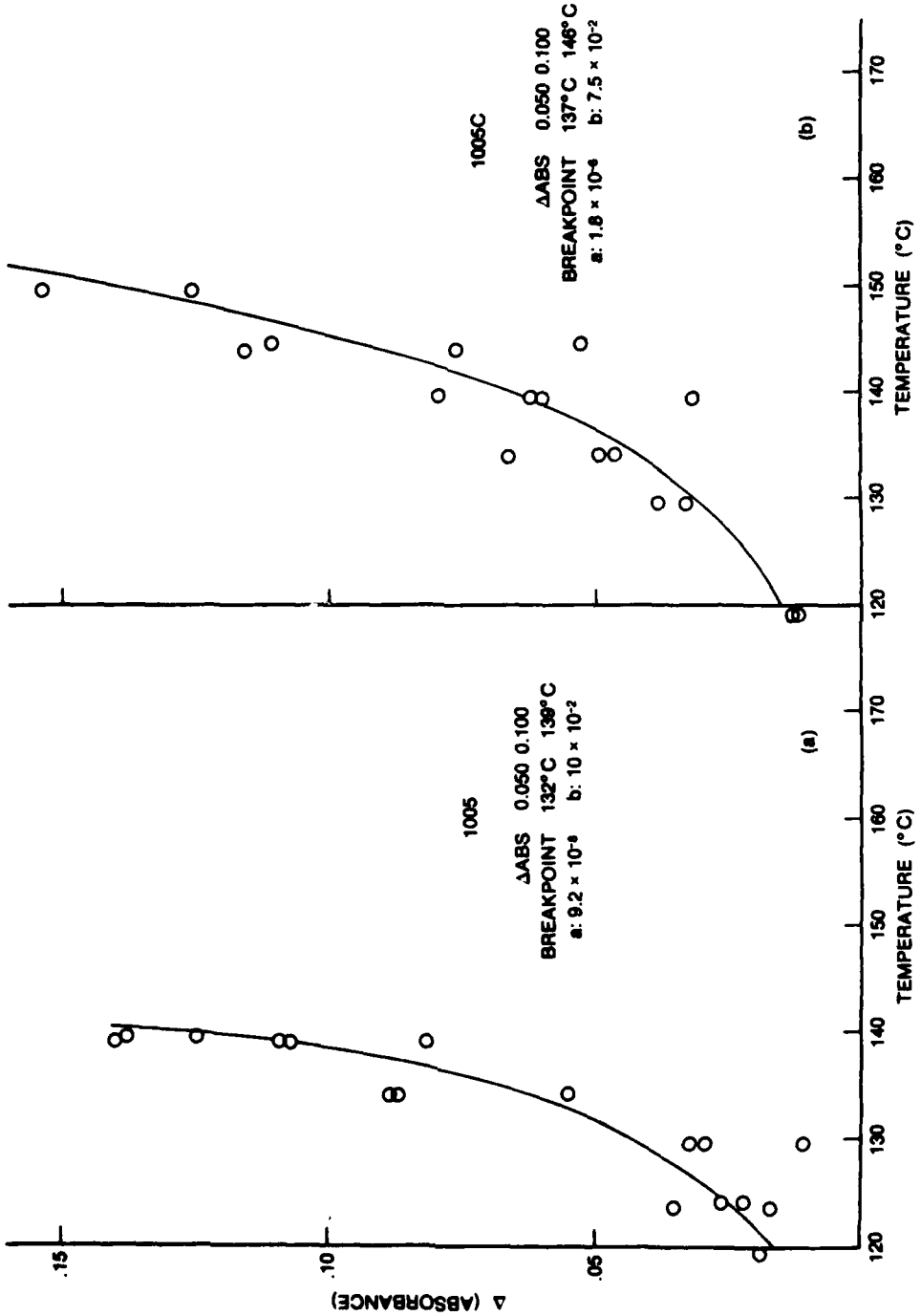


FIGURE 9 - (a) As Fig. 5(a) for 1005 as Received (b) As Fig. 5(a) for 1005 After Clay Filtering

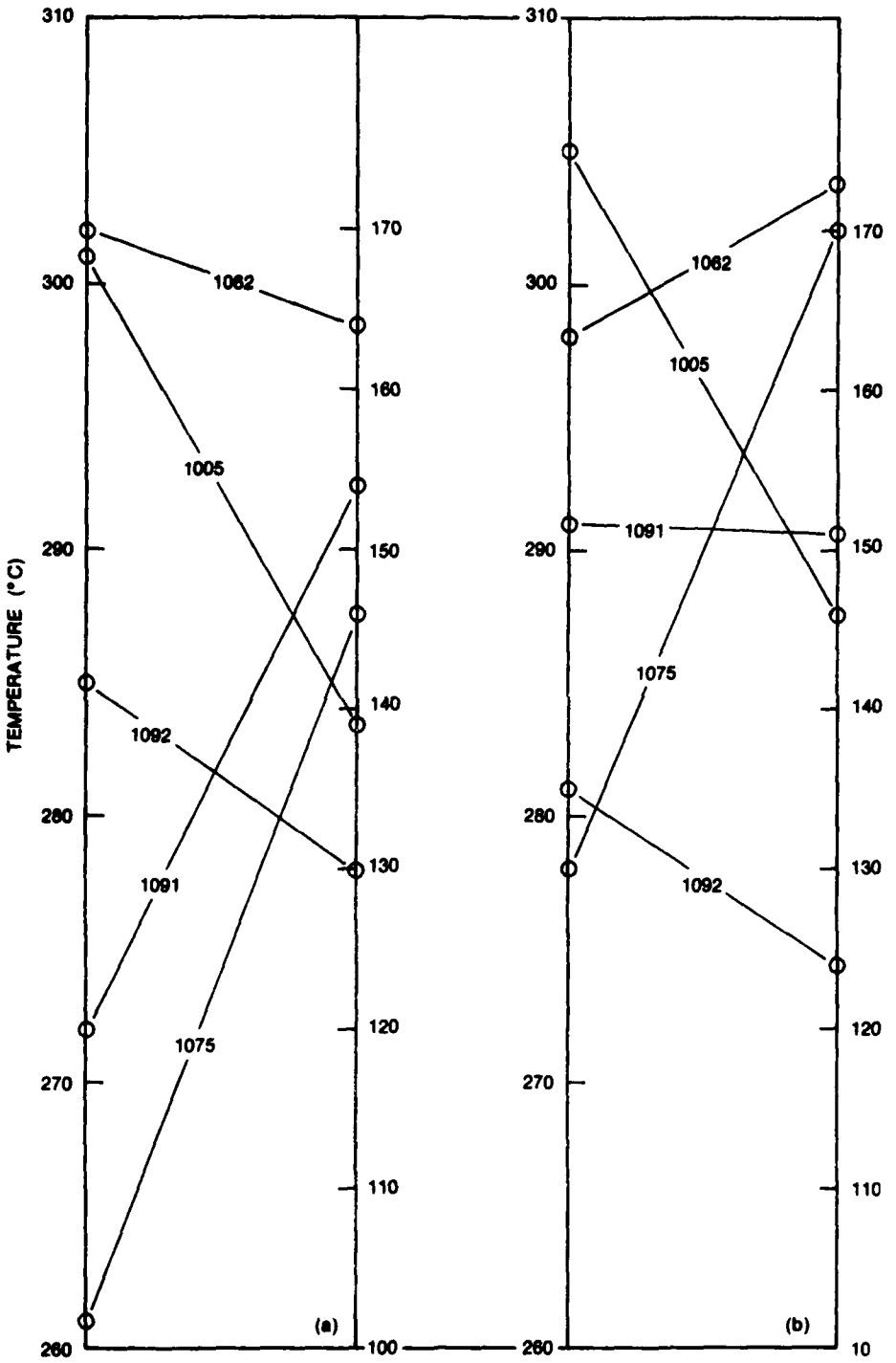
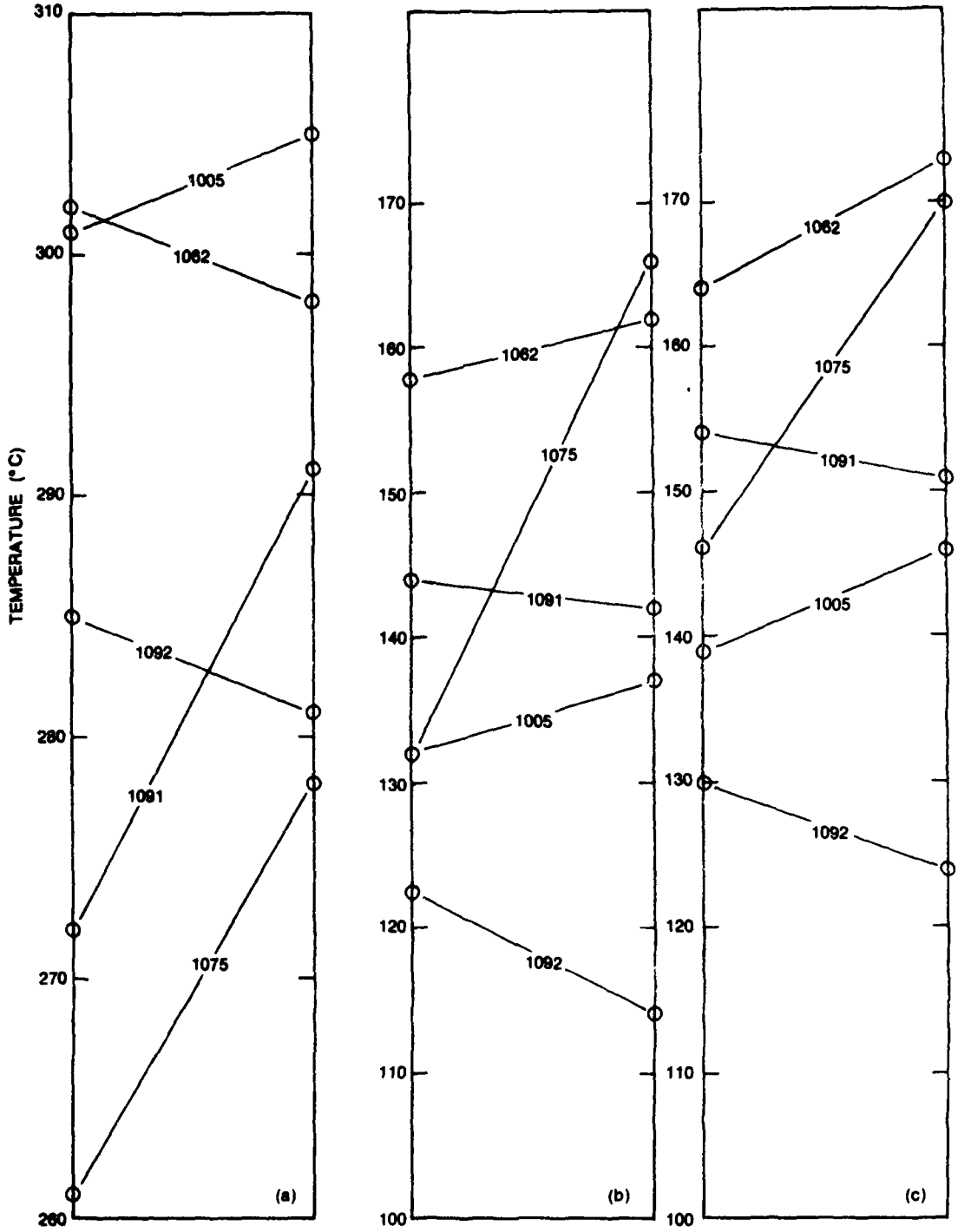


FIGURE 10 - (a) Comparison of Breakpoints by JFTOT (left hand ordinate) and Absorbance Change (right hand ordinate) for Five Fuels, as Received (b) As in Fig. 10(a), for Five Fuels After Clay Filtering



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1 ORIGINATING ACTIVITY Defence Research Establishment Ottawa Ottawa, Ontario CANADA, K1A 0Z4	2a. DOCUMENT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. DOCUMENT TITLE

COMPARISON OF JFTOT AND ABSORBANCE METHODS FOR DETERMINING JET FUEL THERMAL STABILITY

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

TECHNICAL NOTE

5. AUTHOR(S) (Last name, first name, middle initial)

Coleman J.R. and Gallop L.D.

6. DOCUMENT DATE DECEMBER 1983	7a. TOTAL NO. OF PAGES 17	7b. NO. OF REFS 6
8a. PROJECT OR GRANT NO. 25B	9a. ORIGINATOR'S DOCUMENT NUMBER(S) DREO TN 83-34	
8b. CONTRACT NO.	9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document)	

10. DISTRIBUTION STATEMENT

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11. SUPPLEMENTARY NOTES	12. SPONSORING ACTIVITY DREO

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KEY WORDS

Jet Fuel

Thermal Stability

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